HYDRAZINE COMPLEXES OF METAL HYDROXY NAPHTHOATES – NEW PRECURSORS FOR METAL OXIDES

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ABSTRACT

Reaction of hydrazine and 3-hydroxy-2-naphthoic acid with some transition metal ions forms complexes of the type $[M(N_2H_4)_2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$where M = Cd, Zn, Cu and Mn in alcoholic medium. Analytical data confirms the compositions of the complexes. The acid shows dianionic nature in these complexes. IR data indicates the nature of hydrazine in the complexes. Simultaneous TG-DTA studies shows thermal degradation patterns for the complexes. All the complexes follows uniform degradation pattern with the respective metal hydroxy naphthoate as intermediates. The final products is found to be metal oxides of nano size. The surface morphology and quantative analysis of metal oxides were determined by using SEM analysis. The shape of the nano zinc oxide is rock like hexagonal structure while that of nano Mn oxide is rod like structure which was confirmed by Transmission Electron microscopy analysis.

KEY WORDS: Hydrazine complexes; 3-hydroxy-2- naphthoic acid ; IR, Thermal analysis.

1. INTRODUCTION

Hydrazine complexes of the first row transition metal ions with a variety of carboxylic acids have been reported in the literature. These include simple aliphatic mono and dicarboxylic acids, [Sivasankar et al.,1997 & Yasodhai et al., 1999] aromatic mono and di carboxylic acids [Kuppusamy et al. 1996 & Kuppusamy et al., 1995] and heterocyclic carboxylic acids [Premkumar et al., 2003]. The hydrazinium metal carboxylates [Vairam et al., 2006] and their hydrates are crystalline solids and mostly water soluble but hydrazine complexes are amorphous powder and are insoluble in water. Many bis-hydrazine and hydrazinium metal carboxylates are used as precursors for metal oxides and mixed metal oxides such as ferrites, cobaltites, chromites etc [Ravindranathan et al., 1987].

3-hydroxy-2-naphthoic acid is a best example in a naphthalene derivative that has been frequently used as the chelating agent. Bin Liu et al prepared Cr (III) complex with this chelating agent [Bin Liu et al., 2007]. Fluorescence property and stability constant have been studied [Rodriguez-Caceres et al.,2005]. In this paper we report the preparation, characterization and thermal decomposition of some new hydrazine complexes with this acid.

2. EXPERIMENTAL

2.1 Preparation of the Complexes

$[M(N_2H_4)_2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$where M = Cd, Zn, Cu and Mn

These compounds were prepared by adding 60ml of the ligand solution containing mixture of alcoholic 3-hydroxy-2-naphthoic acid (0.188g ; 1m mol) and hydrazine hydrate (0.1 g ;2m mol) to 20 ml of an aqueous solution of the respective metal nitrate at pH 6. The solution which appeared cloudy at first, turned out to be a micro crystalline solid on digestion by keeping it over a hot water bath at 90°C. It was cooled, filtered washed with distilled water, ethanol and then with ether and dried in a desiccator over anhydrous $CaCl_2$. All the complexes obtained are microcrystalline solids, which are stable in air and insensitive to light. They are insoluble in water and in common organic solvents like ethanol, acetone and chloroform. The analytical data of the complexes are compatible with the proposed composition for the complexes.

2.2 Physicochemical Techniques

The compositions of the complexes were fixed by chemical analysis and confirmed by micro elemental analysis. Hydrazine content was determined by titrating against standard KIO_3(0.025mol L^{-1}) under Andrew's conditions. Metal Contents were determined by titrating with EDTA (0.01mol L^{-1}) after decomposing the complexes with 1:1 nitric acid [Vogel 1975].

IR spectra of the complexes in the region 4000-400 cm^{-1} were recorded as KBr pellets using a Perkin Elmer 597 spectrophotometer. The X-ray powder patterns of the complexes were recorded using a Philips X-ray diffractometer (model PW 1050/70) employing Cu-Kα radiation with a nickel filter. The simultaneous TG-DTA experiments were carried out using SDT Q600 V8.3 instrument and Stanton 781 simultaneous thermal analyzer. Thermal analyses were carried out in air at the heating rate of 10 °C min^{-1} using 5 to 10 mg of the samples. Platinum cups were employed as sample holders and alumina as reference. The temperature range was ambient to 700 °C. The SEM images of the residual oxides were recorded using a Cambridge Scanning Electron Microscope with EDAX attachment (CF).

3. RESULTS AND DISCUSSION

3.1 IR spectra of complexes

The N-N stretching frequencies (Table1) observed in the range 1144-1235 cm-1 are the evidence for the presence of coordinated N_2H_4 [Braibanti et al., 1968] in the complexes which were not found for free acid. The carbonyl stretching frequency, which appears as a strong band at 1685 cm-1 in the free acid, vanishes upon the formation of the complex, indicating that the carboxylic groups are all deprotonated. In all the complexes the asymmetric and symmetric stretching frequencies of the carboxylate ions are seen in the range 1596-1678 cm-1 and 1304-1388 cm-1, respectively, with an average separation of (Δv = vasy - vsym) in the range 251-374 cm -1, indicating the monodentate coordination of carboxylate group [Nakamoto 2009]. The peak in the range 460-476 cm-1 is ascribed to the characteristic vibration of M-O bond [Deacon et al., 1980].

3.2 Thermal Analysis

The TG – DTA experiment was carried out to explore the thermal stability of the complexes. The different decomposition stages of the complexes with percentage loss are represented in Table 2.

The compositions of the intermediates and the final products are those which best fit with the observed mass losses in the TG studies. Thermogravimetric results are in good agreement with the DTA data. As a representative example, TG-DTA of $[Zn(N_2H_4)_2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]]$ is shown in Fig. 1.

This complex undergoes complete decomposition from 148 – 206 ºC showing a endotherm at 200 ºC implying the elimination of water and hydrazine, and a broad enotherm centered at 481 ºC due to oxidative decomposition of organic moiety to give the respective metal oxides as the final residue. XRD pattern of which were found to be conforming to those of metal oxides reported in Joint Committee Powder Diffraction Standards for analysis. While comparing with the thermal behaviour of pure acid, it is understood that the decomposition of the hydrazine complex occurs at much lower temperature than that of pure acid. This may be probably because of the fuel nature of hydrazine.

When the temperature of decomposition of transition metal complexes of benzoic acid is compared with naphthoic acid complexes, it was found that decomposition temperature of benzoic acid complexes is less than the corresponding naphthoic acid complexes. This may be obviously due to the fact that naphthoic acid is the higher homologue of benzoic acid.

3.3 Scanning electron microscopy

The metal oxides formed after the incineration of the complexes at their decomposition points found from DTA, followed by sintering at the same temperature for about 3 -4 hours were found to be pure and uniform in nano scale (30-50 nm) as noted from XRD using Scherer's formula [Guozhong Cao et al., 2004]. The oxides obtained in this way are expected to be chemically more homogeneous, free of contamination by impurities and highly reactive. As a representative example, image of ZnO from SEM is shown in Fig. 2. In the EDAX analysis, no additional peaks were observed (Fig. 3), and the peaks are due to Zinc oxide which indicates that the prepared Nano metal oxide is pure and is free from other precursors like H, N, S etc.

3.4 Transmission electron mocroscopy

TEM analysis of cross-sectional samples was carried out for the prepared nanometal oxides. It was apparent from the Fig.4 that the metal oxides are in

good distribution with evenness and there is formation of agglomerates.

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Table 1 Analytical Data and IR spectra of the Complexes

Molecular Formula of Complexes	Colour	D.pt/ °C	Hyrazine Fd. (calcd.)	Metal Fd. (calcd.)	υC=O asym cm^{-1}	υC=O sym cm^{-1}	υ asy- υ sy cm^{-1}	υ M-O cm^{-1}	υ N –N cm^{-1}	υ NH cm^{-1}
$[Cd(N_2H_4)2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$	Green	135	17.54 (17.65)	30.89 (31.01)	1596 (m)	1316 (s)	280	466 (s)	1144 (m)	3290 (s)
$[Zn(N_2H_4)_2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$	Dull white	180	20.21 (20.29)	20.65 (20.73)	1678 (m)	1304 (m)	374	476 (s)	1175 (m)	3267 (s)
$[Cu(N_2H_4)_2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$	Blue	67	20.37 (20.41)	20.13 (20.26)	1646 (m)	1312 (s)	334	470 (s)	1178 (m)	3288 (s)
$[Mn(N_2H_4)_2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$	Brown	165	20.87 (20.92)	18.19 (18.25)	1639 (s)	1388 (s)	251	472 (s)	1235 (m)	3259 (m)

Table 2 Thermal Analysis of the complexes

Molecular formula of the complexes	DTA peak Temp (°C)	TG			Decomposition products
		Temp. Range (°C)	Weight loss%		
			obsd.	calcd.	
$(N_2H_4)_2\ [Cd\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$	291 (-)	270- 320	17.65	17.43	$Cd\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}$
	496 (-)	450-700	64.56	63.98	CdO
$(N_2H_4)_2\ [Zn\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$	279 (-)	270- 320	20.29	20.34	$Zn\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}$
	520 (-)	480 - 700	74.19	74.21	ZnO
$(N_2H_4)_2\ [Cu\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$	360 (-)	350-700	76.67	75.89	CuO
$(N_2H_4)_2\ [Mn\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}]$	320 (-)	100 - 237	76.51	76.4	FeO

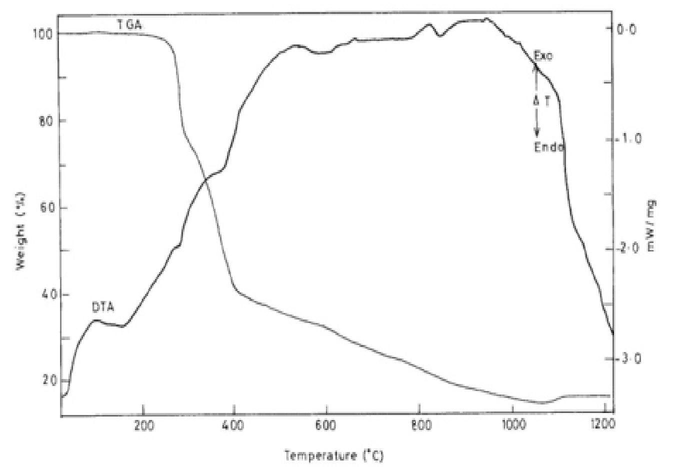

Fig. 1 TG-DTA Curve of Zn complex

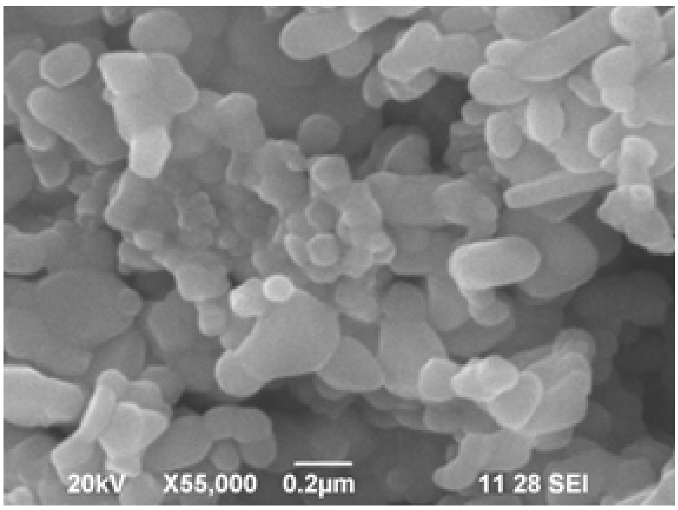

Fig. 2 SEM image of Zn oxide

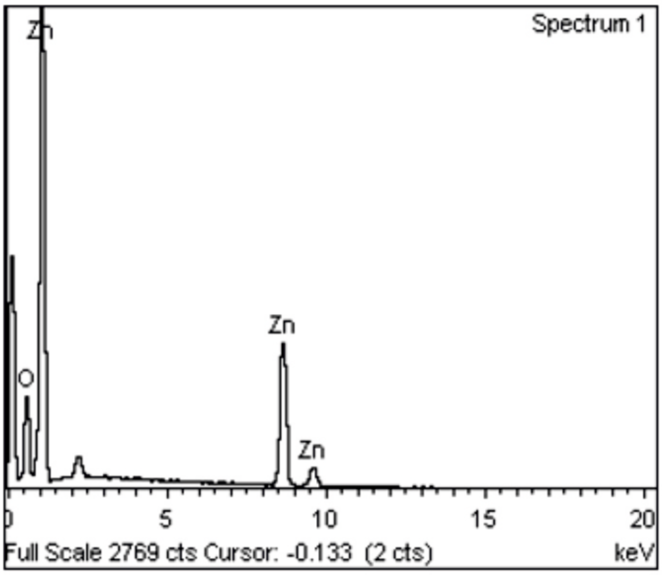

Fig. 3 EDAX of Zinc Oxide

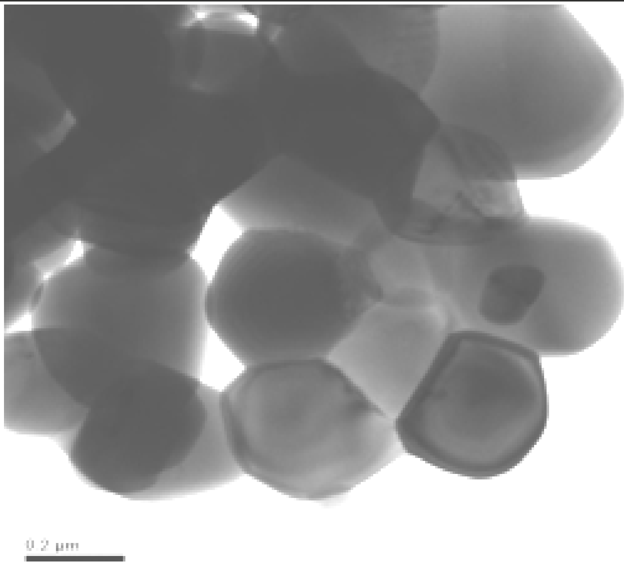

Fig. 4 TEM Image of Zn Oxide